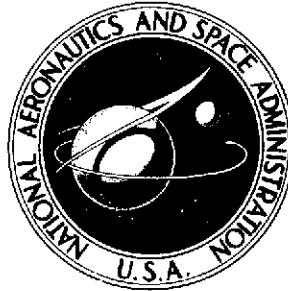


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OXYGEN REDUCTION ON SEVERAL
GOLD ALLOYS IN 1-MOLAR
POTASSIUM HYDROXIDE

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16. Abstract <p>With rotated disk-and-ring equipment, polarograms and other electrochemical measurements were made of oxygen reduction in 1-molar potassium hydroxide on an equiatomic gold-copper (Au-Cu) alloy and a Au-Cu alloy doped with either indium (In) or cobalt (Co) and on Au doped with either nickel (Ni) or platinum (Pt). The results were compared with those for pure Au and pure Pt. The two-electron reaction dominated on all Au alloys as it did on Au. The polarographic results at lower polarization potentials were compared, assuming exclusively a two-step reduction. A qualified ranking of cathodic electrocatalytic activity on the freshly polished reduced disks was indicated: anodized Au > Au-Cu-In > Au-Cu > Au-Cu-Co ≈ Au-Pt > Au-Ni. Aging in distilled water improved the electrocatalytic efficiency of Au-Cu-Co, Au-Cu, and (to a lesser extent) Au-Cu-In.</p>			
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SUMMARY

With rotated disk-and-ring equipment, polarograms and other electrochemical measurements were made of oxygen reduction in 1-molar potassium hydroxide on an equi-atomic gold-copper (Au-Cu) alloy and a Au-Cu alloy doped with either indium (In) or cobalt (Co) and on Au doped with either nickel (Ni) or platinum (Pt). The results were compared with those for pure Au and pure Pt. The two-electron reaction dominated on all Au alloys as it did on Au. The polarographic results at lower polarization potentials were compared, assuming exclusively a two-step reduction. A qualified ranking of cathodic electrocatalytic activity on the freshly polished reduced disks was indicated: anodized Au > Au-Cu-In > Au-Cu > Au-Cu-Co \approx Au-Pt > Au-Ni. Aging in distilled water improved the electrocatalytic efficiency of Au-Cu-Co, Au-Cu, and (to a lesser extent) Au-Cu-In.

INTRODUCTION

Research under several NASA-sponsored contracts has indicated that certain gold alloys may have desirable characteristics as oxygen (O_2) electrocatalysts in alkaline solutions. In particular, Bocciarelli (ref. 1) has suggested that gold-copper (Au-Cu) alloys when doped with divalent and trivalent metals may excel pure platinum (Pt) or pure Au. Other work (ref. 2) has suggested that Au doped with Pt or other metals is a superior electrocatalyst. This improvement results from a combination of changes, both electrochemical and physical. In order to elucidate the electrochemical aspects involved, the present study of O_2 reduction in "gettered" 1-molar potassium hydroxide (KOH) was done by using the rotated disk-and-ring method with well-characterized Au-alloy disks. The alloys were equiatomic Au-Cu, Au-Cu doped with either indium (In) or cobalt (Co), and Au doped with either Pt or nickel (Ni). The data obtained are compared in this report with data for pure Au and Pt.

Most of the primary data are disk current i or ring current i_R obtained from slow triangular sweeps of the disk potential E from -0.2 to 1.2 volts relative to the saturated hydrogen electrode potential in the same solution (SHE-ss). Several times during the investigation the disks were examined by rapid-sweep voltammetry and by capacitance measurements (current-step method). The latter was an attempt to monitor the surface area. All the metals were electrochemically characterized after they were freshly polished, and Au-Cu, Au-Cu-In, Au-Cu-Co, and pure Au were also characterized after they had been stored in distilled water (H_2O) for several months.

EXPERIMENTAL APPARATUS AND PROCEDURE

All data were obtained in a rotated-disk-and-ring apparatus developed and fabricated at Case Western Reserve University (ref. 3, p. 30).

Experimental Electrodes

Nominal atomic compositions of the disks used in the rotated-disk electrodes are given in table I. The Au-Cu, Au-Cu-In, and Au-Cu-Co alloys were prepared and characterized as to phases present by Professor D. Robert Hay of Drexel University. They were cast and quickly cooled as cylindrical pellets, 6 millimeters in diameter by 13 millimeters. They were not annealed. The quick cooling was done to duplicate as closely as possible in a small pellet the shot-tower preparative method of C. F. Bocciarelli (ref. 1).

The quickly cooled Au-Cu-In alloy used in the present work was a cored structure, 80 percent by volume in an amorphous matrix. X-ray diffraction of the powdered material indicated a single face-centered cubic (fcc) phase. (Upon annealing, the Au-Cu-In alloy changed to a two-phase structure, the second phase occupying 7 percent of the volume.)

The Au-Cu-Co alloy had a dendritic Co-rich second phase, 3 percent by volume, as shown by optical-metallographic and scanning-electron microscopy. Microprobe analysis indicated uniform composition in both the In- and the Co-doped alloys.

The alloys Au-Ni and Au-Pt were prepared and characterized at the Lewis Research Center. They were cast from high-purity metals (99.999-percent-pure Au), swaged, and annealed; both were fcc single phase.

Disks of the rotating electrodes were fabricated from the five alloys (table I) and pure Au (99.999-percent purity). The ring electrode of each was 99.999-percent-pure Au. The approximate radii of a disk and a ring were 2.54, 2.80, and 3.58 millimeters. (Exact dimensions of each electrode were measured, and these were used to reduce the

electrochemical data.) A disk and a ring electrode of high-purity Pt (99.999-percent-pure) of similar dimensions was also assembled, and this was used for purposes of comparison.

Each assembled electrode was hand polished to an optimum mirrorlike surface on separate new cloths with fresh alumina powder and distilled water (finishing with 0.05- μm powder). Some variations in the polishing were developed to accommodate differences in hardness. Each electrode was cleaned after polishing by being rotated against a tuft of new borosilicate glass wool contained in a beaker of fresh 1-molar KOH. Each electrode was then rotated in several washes of distilled water. The original practice was to store the electrodes in distilled water which was changed at least each time they were used. Later practice was to spin the electrodes dry in air after several rinses in distilled H_2O and to store them in a dry argon atmosphere.

Electrolyte

The 1-molar KOH was always prepared from reagent grade KOH and freshly boiled distilled water. The first batches of 1-molar KOH were stored in borosilicate glass, but later batches were kept in a polytetrafluoroethylene (TFE) bottle wrapped tightly with aluminum foil (to prevent diffusion of atmospheric impurities through the TFE).

The only materials to contact the electrolyte in the cell (other than the experimental disk-and-ring electrodes) were the pure-Au gettering and counter electrodes and the TFE cell itself. Originally the cell and the gettering and counter electrodes were soaked in a 1:1 mixture by volume of nitric acid (HNO_3) and sulfuric acid (H_2SO_4) and given several soakings in distilled water and then in dilute KOH. Later in the program, because of possible mercury contamination, the TFE cell was rinsed with aqua regia (but not the electrodes), and the cell was rinsed with distilled water and given several extended soakings in fresh batches of 1-molar KOH.

Before a set of electrochemical determinations was made, about 200 cubic centimeters of 1-molar KOH was transferred into the cell and gettered by means of about 160 square centimeters of 0.13-millimeter-diameter pure Au wire held on a frame of 0.76-millimeter-diameter pure Au wire. The gettering electrode was held potentiostatically at about 0.3 volt relative to the SHE-ss for periods ranging from several days to several hours. The shorter gettering periods were necessitated later in the program after instabilities developed in the control system. The counter electrode was a wattle of 0.76-millimeter-diameter pure Au wire about 60 square centimeters in area.

Instrumentation

In the polarographic and rapid-sweep voltammetric determinations, the disk and ring potentials (E and E_R , respectively) were controlled by a dual potentiostat which was based on the design of reference 4 and was fabricated at this Center. In these determinations, the control potential of E was swept continuously (alternately in anodic and cathodic directions) with a triangular wave generated by a commercially available instrument. The ring potential E_R was held constant, usually at 1.2 volts anodic to the saturated hydrogen electrode in the same solution (SHE-ss).

In the polarographic determinations, indicated disk and ring currents (i and i_R , respectively) were recorded by two x,y-plotting potentiometers as functions of E . In the rapid-sweep voltammetry determinations, chopped signals from a dual-trace amplifier representing i and i_R were recorded against E as cathode-ray oscillograms. The i_R signal from the dual potentiostat was isolated from the oscilloscope ground by a differential amplifier.

In the capacitance determinations, chopped signals representing i and E were recorded against time in cathode-ray oscillographs. A step in i was introduced by either opening or closing a mercury relay, which added a dry cell and some resistances to the circuit. Capacitance was computed from the initial slope of E against time and the step change in i .

The reference electrode used for most of the study was the dynamic hydrogen electrode of Giner (ref. 5). It was calibrated in 1-molar KOH against a mercury/mercuric oxide (Hg/HgO) electrode (separated from it by a ground-glass seal). The correction of -21 millivolts (ref. 5) was corroborated. A commercial Hg/HgO electrode was used initially as a reference, but its use was stopped in favor of the Giner electrode. The cell was thoroughly cleaned after the removal of the Hg/HgO electrode.

RESULTS AND DISCUSSION

Polarograms

Consistently high values of ring current i_R showed at the outset that the two-electron reduction of O_2 (with the formation of O_2H^- as an intermediate) predominated on all the Au alloys studied in this work, as well as on pure Au. (This was not true for the pure Pt electrode, which showed low ring currents.) The dominance of two-electron reduction ($O_2 + 2e^- + H_2O \rightarrow O_2H^- + HO^-$) on pure Au in 0.1-molar KOH has been well established by experimental studies in both the United States and the Soviet Union (e.g., refs. 3 and 6 to 8).

Zurilla and Yeager (ref. 3) did a polarographic-type study on Au and in their analysis assumed no four-electron reduction whatsoever. The net result of their reasoning can be summarized in the following relations:

$$i_1 = \frac{1}{2} \left(i + \frac{i_R}{N} \right) \quad (1)$$

$$\frac{1}{i_1} = \frac{1}{i_{1K}} + \frac{1}{B\omega^{1/2}} \quad (2)$$

where B is a diffusion parameter defined by J. Newman as

$$B = \frac{nFC\nu^{1/2} 0.621 \text{ Sc}^{-2/3}}{1 + 0.298 \text{ Sc}^{-1/3} + 0.145 \text{ Sc}^{-2/3}} ((\text{mA})(\text{cm}^{-2})(\text{sec}^{1/2})) \quad (3)$$

and

- C bulk molar concentration of reactant, moles/cm³
- D diffusion coefficient of reactant, cm²/sec
- F Faraday constant, 9.65×10^7 (mA)(sec)
- i disk current density, mA/cm²
- i_R ring current density, mA/cm²
- i_1 corrected current density for limiting reaction of two-step O₂ reduction, mA/cm²
- i_{1K} electrochemically limited current density, mA/cm²
- N collection efficiency of ring, a function of ring and disk geometry, dimensionless
- n number of electrons transferred per mole of reactant
- Sc Schmidt number, ν/D
- ν kinematic viscosity, cm²/sec
- ω rotational velocity, rad/sec (given in this report as rotations/sec)

In this work the hypothesis represented by equations (1) and (2) was applied to the polarographic results for pure Au and the Au alloys. Accordingly, from equation (2), the current i_{1K} is electrochemically limited and should be a criterion of electrocatalytic activity at a given E . For any one metal at fixed temperature and O₂ pressure in a given electrolyte, a plot of $\log i_{1K}$ against E should give a line of one or more "Tafel slopes."

In the present work values of i_{1K} at selected values of disk potential E for each metal were computed by two methods. In the first i_{1K} was computed directly from i_1 (eq. (2)) for four values of velocity ω by using a value of $B = 0.122$ milliamperes second^{1/2} per square centimeter; B was obtained from equation (3) for $C = 0.806 \times 10^{-6}$ mole per cubic centimeter, $D = 1.49 \times 10^{-5}$ square centimeter per second (ref. 9, pp. 32 and 108), and $\nu = 0.0098$ square centimeter per second (ref. 10). The other approach was to evaluate i_{1K} and B by a least-squares fit of $1/i_1$ as a function of $1/\omega$ (eq. (2)). Values of N (eq. (1)) were obtained from Alberly and Bruckenstein (ref. 11).

Figures 1 to 4 are Tafel-type plots of E against i_{1K} on a log scale. The data points represent i_{1K} values computed by the first method ($B = 0.122$ (mA) (sec^{1/2}) (cm⁻²)) from i and i_R at ω of 15, 30, 60, and 120 rotations per second. A fifth set of points is i_{1K} from least-squares fit. Selection of a standard of comparison by means of these plots is discussed in the next section. Then the assumed electrochemically limited two-step reduction of O_2 on the reduced freshly polished surface of each alloy is compared with the selected standard. The effect on this reaction of aging the surfaces of the three Au-Cu alloys is considered next, and finally an overall assessment is made of electrochemical effects due to the metallic composition of the five alloys.

Selection of a standard of comparison. - In this work polarograms were obtained for pure Au that had been treated in three different ways: (1) freshly polished, (2) freshly polished and inadvertently anodized, and (3) not anodized but aged in distilled water for several months. (The anodization resulted from uncontrolled excursions of potential during a momentary unstable coupling between the freshly polished Au and the dual potentiostat.)

The surface of the Au disk that was anodized showed a satiny finish and a slightly reddish coloration. The anodized disk gave the best i_{1K} agreement of the pure gold electrodes. Figure 1(a) shows the significant portion of these results for the anodic-direction sweep up from -0.20 volt relative to SHE-ss. The agreement is excellent to fair from 0.9 to 1.04 volts. The principal slope is approximately 0.05 volt per decade (one-half of the slope that a one-electron-limited reaction with a transfer coefficient of 0.5 should show). A less-steep slope above 1.02 volt seems to be indicated. At $E < 0.9$ volt a significant variation in slope can be seen; the i_{1K} computed from the i and i_R at lower ω seem to follow a slightly steeper slope than at $E > 0.9$ volt, but a definitely steeper slope is shown by results from higher ω (120 rotations/sec) and by the least-squares extrapolations. These steeper slopes (roughly averaging 0.1 V/decade are consistent with a one-electron-limited reaction.

Published polarization data for O_2 reduction on Au in 0.1 and 0.125-molar KOH (refs. 3 and 6 to 8) all show greater polarizations (lower potentials) than were obtained in this work with 1-molar KOH. Experiments and theoretical thermodynamic considerations (ref. 6) have shown that an increase in KOH concentration from 0.1 to 1 molar should reduce the polarization by about 20 to 30 millivolts rather than by over

100 millivolts as in this work. This greater reduction suggests the possibility of an unknown variable in the present work. As discussed in the section Electrochemical Effects of Alloy Composition, lower polarizations (as shown in the present work) are typical of conglomerate gold-bearing electrocatalysts. The results of the present work should allow valid comparisons of the relative electrochemical behavior of pure Au and the alloys of this study at OH^- activities approaching those to be found in practical devices.

The results of Zurilla and Yeager (ref. 3) show a change in slope similar to that in figure 1(a) (for 120 cps and the least-squares fits) but at a polarization about 0.13 volt higher (E , 0.13 V lower). Some of their results are closer to the ones shown in this report; they attribute their lower polarization to trace impurities of Pt in the electrolyte. In the present work a conscientious effort was made to avoid Pt contamination. (Also, as shown in the next section, the addition of Pt to pure Au did not seem to increase Au electrocatalytic activity.)

Figure 1(b) shows the same kind of plot as figure 1(a) and is for anodized pure gold; however, i_{1K} is computed from i and i_R obtained in a cathodic-direction sweep down from 1.2 volts relative to SHE-ss. The slope at 0.95 to 1.04 volts (approximately 0.04 V/decade) is less steep than that from the anodic sweep (fig. 1(a), shown by the dashed line), and the currents are higher at approximately 0.95 volt. The agreement is better than in figure 1(a) at 0.8 to 0.9 volt, where a steeper slope is again indicated. The more consistent steeper slope for the nonreduced-electrode (cathodic sweep direction) corroborates the finding of Zurilla and Yeager (ref. 3) that consistency of the polarographic data is improved by staying away from the more-cathodic potentials.

Figure 1(c) shows the same kind of plot as figures 1(a) and (b), but for aged pure Au (anodic sweep direction, up from -0.2 V). The data points for the aged Au show more scatter than the ones for the anodized Au. These data do seem to define an upper limit that is close to the line representing the anodized gold (fig. 1(a)). The variation is believed to be due in part to a time factor. The nonanodized pure Au is much slower to reach a steady state than is the anodized Au; the lower points are believed to be from polarograms that were made while the electrode was still "conditioning" itself.

The anodized pure Au did not seem to require a long conditioning period; there seemed to be a "permanent" surface conditioning in this electrode that was beneficial. Because of relatively high precision (which indicated a short conditioning time) and low polarization, the anodized pure Au was selected as a standard of comparison for the Au alloys. The comparisons to follow are all from data obtained in anodic sweeps (i. e., toward more-anodic potentials, up from -0.2 V), because the reduced metal surface state presumably shows more clearly the effects of metallic composition than would an oxidized surface. First, the electrocatalytic behavior of the freshly polished metals is compared; then the effect of aging is considered.

Behavior of freshly polished alloys. - Plots of $\log i_{1K}$ against E , swept in the anodic direction up from -0.2 volt relative to SHE-ss, for all the freshly polished Au

alloys are shown in figure 2. The solid lines are considered to be the best fit of all the plotted data; for comparison, the dashed lines (from fig. 1(a)) show the selected fit of the data from anodized pure Au (swept up from -0.2 V relative to SHE-ss).

The i_{1K} data for freshly polished Au-Cu (fig. 2(a)) mostly fall short of those for pure anodized Au.

For freshly polished Au-Cu-In (fig. 2(b)) the variation in computed i_{1K} is unusually large, but the data agree well at the higher rotational speeds (60 and 120 rps). These currents fall short of those for anodized Au by, say, 20 percent.

Freshly polished Au-Cu-Co (fig. 2(c)) also shows good agreement of i_{1K} from polarograms at 60 and 120 rps (0.9 to 1.04 V), but these currents are only one-half of those from anodized Au. As shown in the next section, however, the electrocatalytic performance of aged Au-Cu-Co is much better.

If the successive two-step reduction model is correct for freshly polished Au-Ni, the presence of 3 percent Ni is deleterious. As shown by figure 2(d), i_{1K} for this alloy is roughly only one-quarter that for pure anodized Au at the higher potentials (approximately 1 V relative to SHE-ss). It would be interesting to see whether or not aging would improve the electrochemical behavior of Ni-doped Au.

The i_{1K} values for freshly polished Au doped with Pt agree moderately well, as figure 2(e) shows. The currents, however, are roughly one-third those for anodized Au. The i_{1K} data for cathodic-direction sweeps (down from 1.2 V relative to SHE-ss) are not shown, but they are similar to the data in figure 2(e) and are more self-consistent. Platinum-doped Au is the only metal in this study that showed nearly identical behavior in both anodic and cathodic sweep directions (at the higher potentials).

Effect of aging. - The aged pure nonanodized Au is discussed in foregoing paragraphs and is compared with freshly polished anodized Au in figure 1(c). The performance (not shown) of freshly polished nonanodized pure Au is similar to that of the aged nonanodized pure Au in figure 1(c), except that the newly polished Au shows somewhat less downward variation.

The effects of aging on the electrochemistry of the three Au-Cu alloys in anodic-direction sweeps are shown in figure 3. The data points are for the aged disk of an alloy, and the dashed lines are for the freshly polished disk of the same alloy (fig. 2).

Aging improves somewhat the electrochemical performance of each of the three alloys at the higher potentials (0.9 to 1.04 V relative to SHE-ss), the least improvement being in Au-Cu-In (fig. 3(b)). The general improvement is indicated both by higher currents and by closer agreement, particularly for Au-Cu-Co (fig. 3(c)). Aging of Au-Cu-In (fig. 3(b)), however, seems to have reduced the current density in the potential range 0.80 to 0.9 volt relative to SHE-ss. The general improvement in electrochemical efficiency of these alloys by aging is confirmed (perhaps to a lesser extent) by the cathodic-direction sweep data (not shown). The best improvement in electrochemical efficiency due to aging is in the alloy Au-Cu-Co.

Electrochemical effects of alloy composition. - The polarographic data, discussed in the preceding paragraphs, show that the mode of treatment of the Au alloy has effects on electrochemical efficiency which all but mask the effects attributable to alloy composition. Nevertheless, some provisional judgments based on the two-step reduction model are attempted in this section relative to the effect of composition on experimental current densities. To make this comparison, anodic-direction sweeps on freshly polished metals are chosen, because the bright reduced surface should show the least distortion of those effects that are due to metallic composition. Figure 4 facilitates a comparison of the data presented in figure 2.

Some results of Bocciarelli (e.g., fig. 3 of ref. 1) show that in a composite anode Co-doped Au-Cu is remarkably superior to Al-doped Au-Cu in terms of both polarization ($\sim 1/2$ V less) and current density. The present work (fig. 4), however, shows a much smaller difference in cathodic performance of bright Au-Cu due to doping. In terms of polarization, the indicated improvement due to In (a group IIIB element, as is aluminum) and the degradation due to Co are each of the order of 10 millivolts. These differences are close to the possible error in the x, y-recorders and are subject to judgments (noted in the foregoing discussion) on how the lines are drawn. The results in figure 4 do show that Au-Cu may have promise as a good electrocatalyst for the reduction of O_2 in KOH. Although the possibility of selective dissolution of Cu from a Au-Cu cathode in KOH was not completely explored in the present work, no such dissolution was indicated.

Freshly polished Pt-doped Au (fig. 4) behaves about the same as freshly polished Co-doped Au-Cu. By the same criterion, freshly polished Ni-doped Au is the poorest electrocatalyst. It is a bit surprising that Pt-doped Au does not appear better in this comparison.

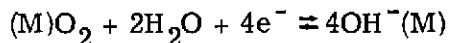
In general, the results shown by figure 4 are remarkably similar to those reported in reference 2 (fig. 1) for conglomerate TFE-mixed Au-containing electrocatalysts in 35 percent KOH at 65° C. At potentials between 0.9 and 1.03 volts, the conglomerates show Tafel slopes of roughly 40 millivolts per decade, which indicates the same electrochemical limiting process that figure 4 of this report does. Even more remarkably, the conglomerates show a similar order in relative current density, that is, $Au_2O_3 > Au-Cu > Au-Ni$. In the comparison of conglomerates (ref. 2), however, Pt-doped Au was relatively better than the present work would indicate. The fact that the relative currents are as comparable as they are would indicate good control of total surface area of the respective metals in the conglomerates (ref. 2). The apparent current densities of the conglomerates at 65° C are roughly one thousand times the electrochemically limited current density of the bright metal at room temperature (fig. 4, this work). The large current densities of reference 2 are presumably due mostly to the large surface area available in the conglomerate electrodes.

Capacitances

Capacitances measured by the current-step method show some variation but no consistent trends with respect to electrode composition, aging, or past history of O₂ reduction. The Au-Cu-Co alloy gave the most consistent results, 65±14 microfarad per square centimeter. The average capacitances from all alloys, whether freshly polished or well used, were near this value.

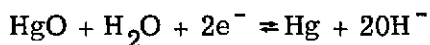
Rapid Sweep Voltammetry

The rapid sweep voltammetry (RSV) determinations, as can be expected, do show some differences among the various pure-metal and alloy disks. It is important to note, furthermore, that RSV results for each metal changed little or not at all as a result of aging or electrochemical operation. Figure 5 shows RSV records for the newly polished disk electrodes of the various metals in 1-molar KOH. All gold-bearing metals (figs. 5(a) to (f)) show important oxidation and reduction peaks starting at approximately 1.2 volts relative to SHE-ss, probably indicating the reaction



where M is the gold-bearing metal. The latter part of the reduction-current peak (approximately 1.0 V) apparently includes also some removal of O₂ from the disk, which is detected by the ring (at 60 cps) when it is held at potentials of about 0.4 volt relative to SHE-ss but not when the ring is at 1.2 volts.

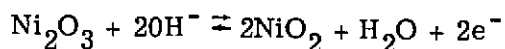
The RSV data for the three copper-bearing alloys Au-Cu, Au-Cu-In, and Au-Cu-Co (figs. 5(b) to (d)) also indicate reversible peaks at 0.93 volt. (These peaks become larger than those shown in fig. 5 after the electrodes stand still in the electrolyte for several minutes.) The potential of 0.93 volt (relative to SHE-ss) could indicate the reaction



The conjecture that a trace of Hg may have been present lead to the following experimental changes: (1) the HgO/Hg reference electrode was removed and replaced with a Giner dynamic hydrogen electrode (ref. 5), (2) the TFE cell was rinsed with aqua regia, (3) the pure Au counter and the gettering electrodes were soaked in a 1:1 mixture of concentrated H₂SO₄ and HNO₃, and (4) the cell and the counter and gettering electrodes were soaked for several days in several changes of 1-molar KOH. The reversible couple at 0.93 volt persisted on all three Au-Cu alloys in spite of this treatment, however, even

after the disk electrodes were repolished separately on new cloths. The size of the reversible peaks at 0.93 volt increased when the disk stood in quiescent 1-molar KOH (data not shown) and diminished when the disk was rotated. The fact that the more pronounced peaks at 0.93 volt occurred with the Cu-bearing alloys suggests a surface-segregation effect. An examination of the Au-Cu and Au-Cu-In alloys by Auger spectroscopy did not show Hg; but any Hg that was present, if loosely held (as it could have been in the electrochemical cell), may well have volatilized in the Auger apparatus. Trace impurities of Hg on the Au-Cu alloys could have come either from the Au or the KOH. Hopefully, the agent causing the redox at 0.93 volt does not seriously affect O₂ reduction on these metals, since rotation of the disk (during E cycling) favored the removal of this material. Inasmuch as there are no pronounced or consistent differences in electrocatalysis between the Cu-bearing alloys and the other gold-bearing disks, this agent probably caused little practical effect.

Another notable RSV effect occurs with a Ni-doped Au disk (both at 0 and 60 rotations/sec), from which sharp oxidation and reduction peaks initiate at a potential of about 1.43 volts relative to SHE-ss (e.g., fig. 5(e)). These peaks may be from the following reaction (which according to ref. 12 would show a potential of 1.434 V measured under these conditions):



where Ni₂O₃ and NiO₂ are nickel sesquioxide and nickel dioxide, respectively.

The Pt-doped Au (fig. 5(f)) produces a voltammogram very similar to that for pure Au (fig. 5(a)) and in no way similar to that for pure Pt (fig. 5(g)). The voltammogram for pure Pt is fairly similar to one found in 0.1-molar sodium hydroxide by Breiter (e.g., ref. 13, p. 49), except that in the present work the oxidation (anodic-direction) sweep shows more detail including three peaks at potentials less than 0.6 volt, perhaps a result of the deeper excursion into the reducing potentials.

SUMMARY OF RESULTS

Five gold (Au) alloys suggested by NASA-sponsored research were evaluated for oxygen reduction characteristics in 1-molar potassium hydroxide (KOH). The alloys were used as rotated disks with pure Au rings, and the results were compared with those for pure Au and platinum (Pt). The principal results were as follows:

1. The two-electron reaction controlled the electrochemistry on the five gold alloys as it does on pure gold.

2. Equimolar Au-copper (Cu) showed promise of being a good cathodic electro-catalyst in KOH.

3. A comparison based on an assumed successive two-step reduction of oxygen suggested the following qualified ranking of cathodic electrocatalytic activity on the bright reduced surface at low overpotential: $\text{Au-Cu-In} > \text{Au-Cu} > \text{Au-Cu-Co} \approx \text{Au-Pt} > \text{Au-Ni}$, where In, Co, and Ni are indium, cobalt, and nickel, respectively.

4. Aging in distilled water improved cathodic electrocatalytic activity of the three Au-Cu alloys. (The effect of aging was not determined for the other two alloys.)

5. Voltammograms were fairly similar for pure Au and the five alloys, although Ni-doped Au indicated strong nickel sesquioxide - nickel dioxide ($\text{Ni}_2\text{O}_3/\text{NiO}_2$) redox peaks.

6. The measured capacitance of all electrodes was roughly 65 microfarads per square centimeter and did not change significantly with aging.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 16, 1975,
506-23.

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TABLE I. - DISK ELECTRODES

Alloy	Atomic fraction					
	Au	Cu	In	Co	Ni	Pt
Pure Au	0.99999	-----	-----	-----	-----	-----
Au-Cu	.518	0.482	-----	-----	-----	-----
Au-Cu-In	.462	.432	0.106	-----	-----	-----
Au-Cu-Co	.488	.456	-----	0.056	-----	-----
Au-Ni	.969	-----	-----	-----	0.031	-----
Au-Pt	.937	-----	-----	-----	-----	0.063--
Pure Pt	-----	-----	-----	-----	-----	.99999

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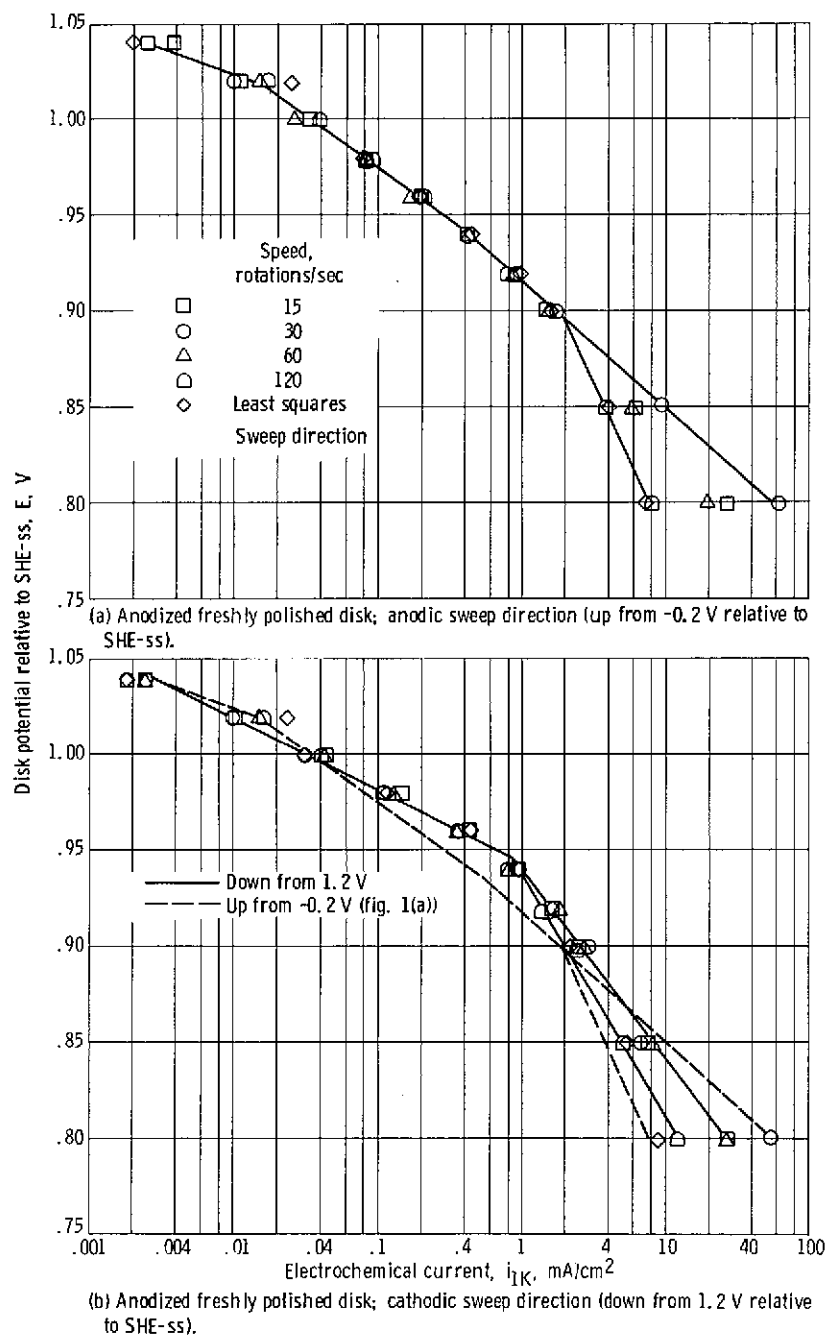
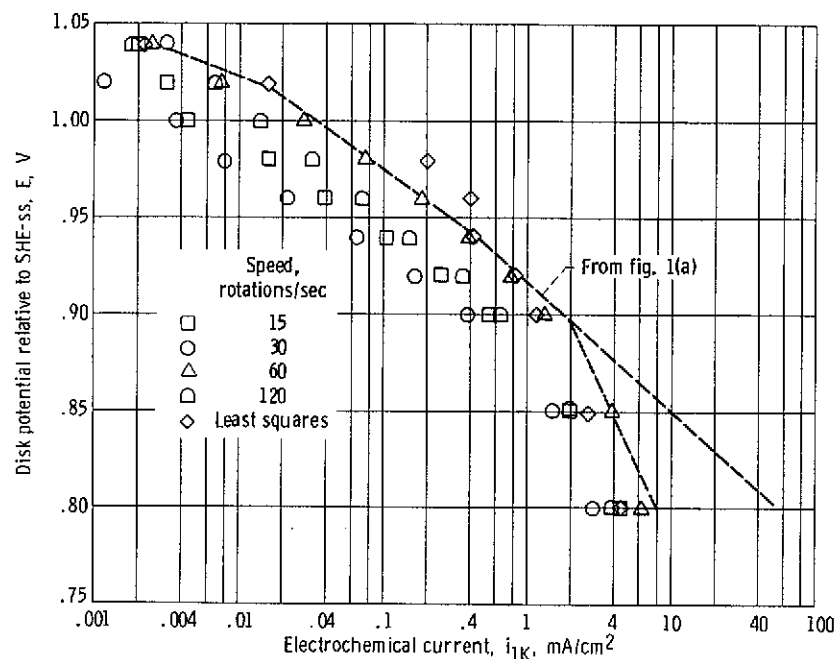


Figure 1. - Tafel plot for pure gold. Two-step reduction model.



(c) Nonanodized aged disk; anodic sweep direction (up from -0.2 V relative to SHE-ss).

Figure 1, - Concluded.

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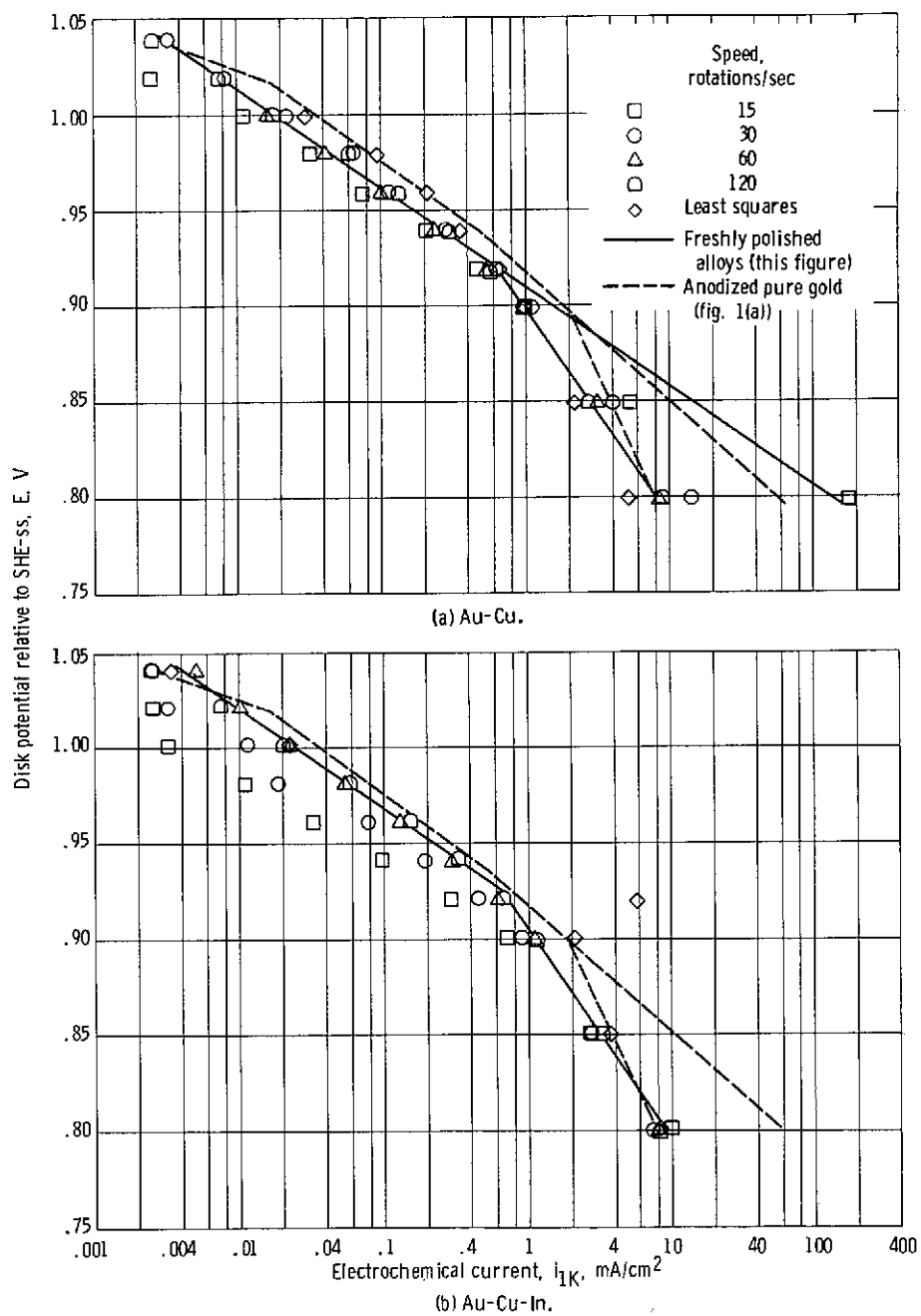
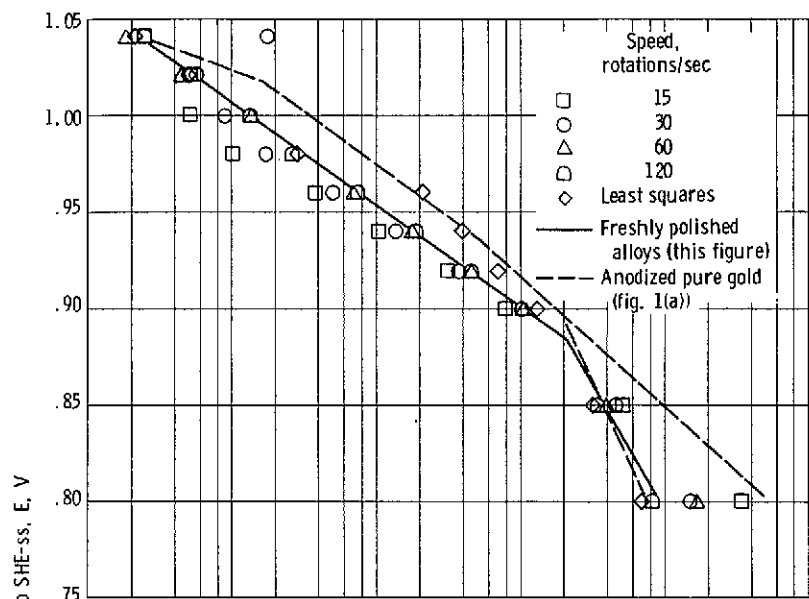
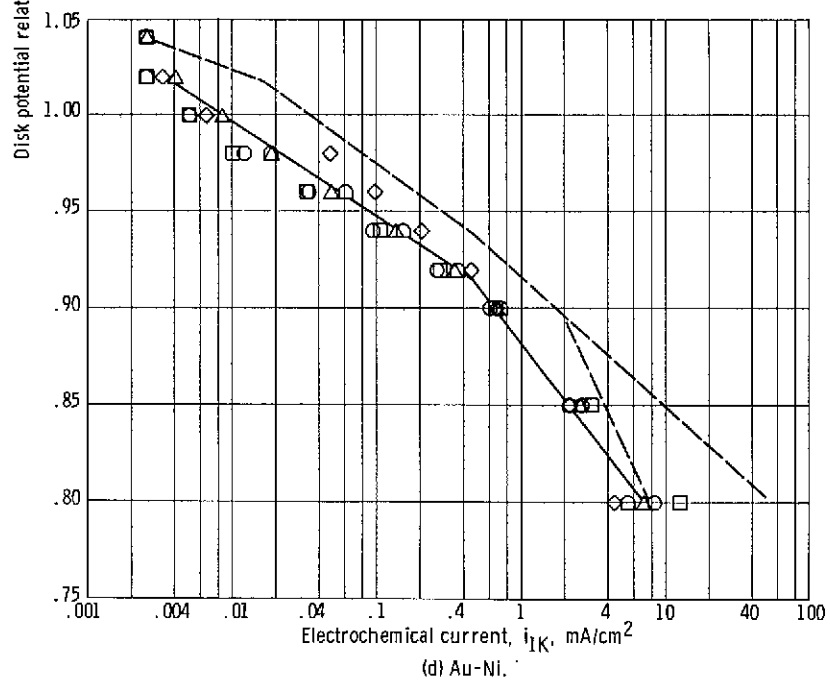


Figure 2. - Tafel plot for freshly polished alloys. Anodic sweep direction.



(c) Au-Cu-Co.



(d) Au-Ni.

Figure 2. - Continued.

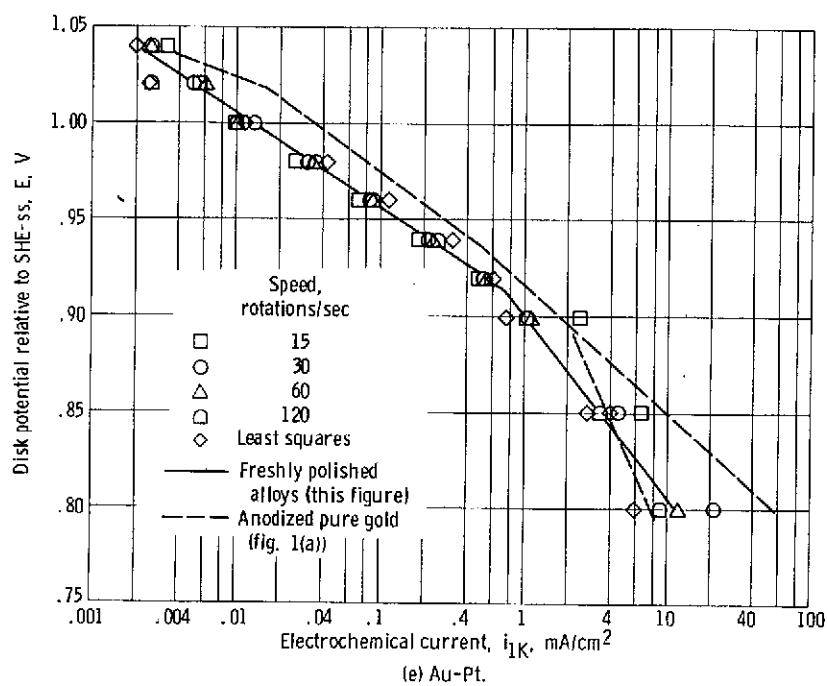


Figure 2. - Concluded.

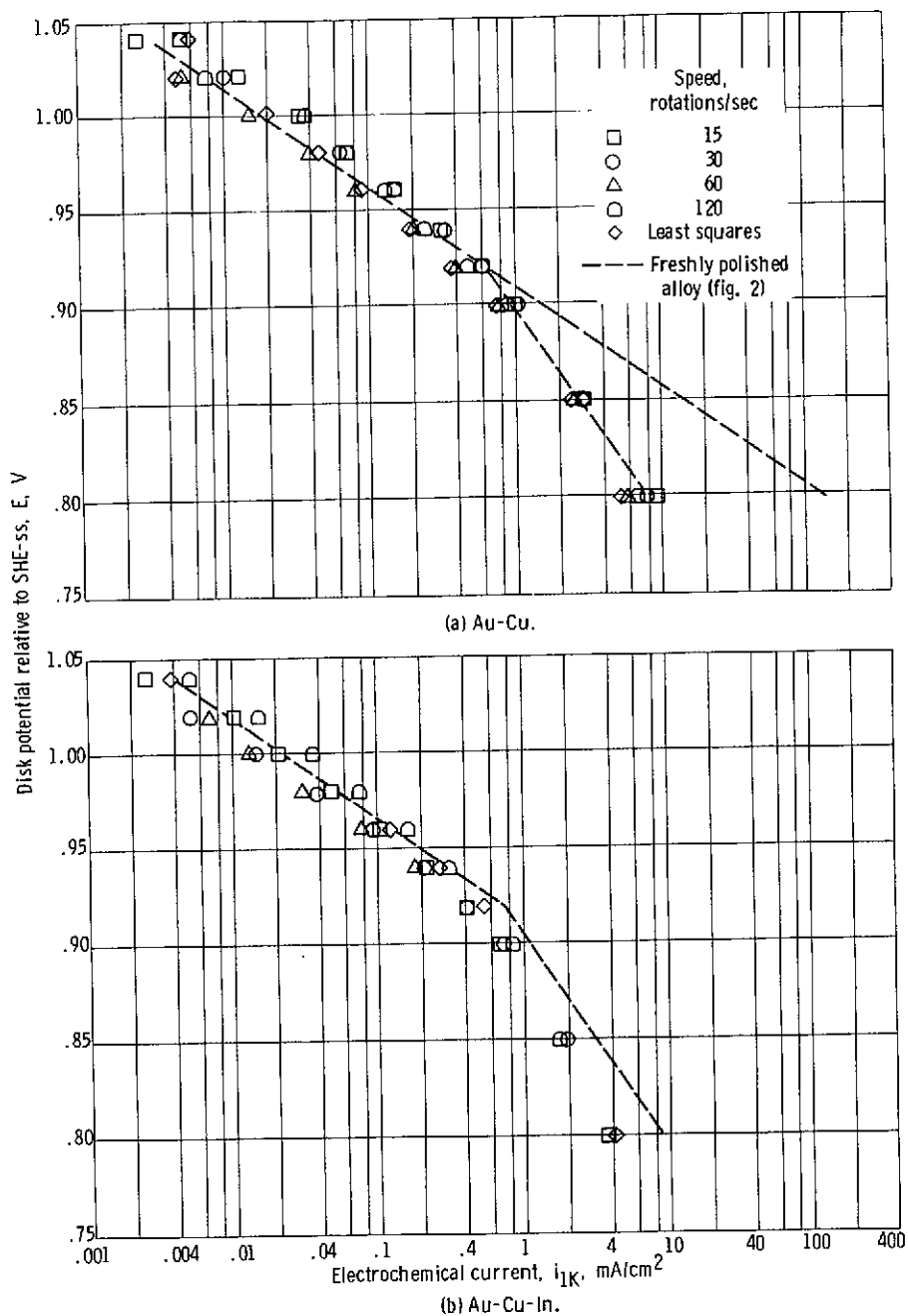


Figure 3. - Tafel plot for aged alloys. Anodic sweep direction.

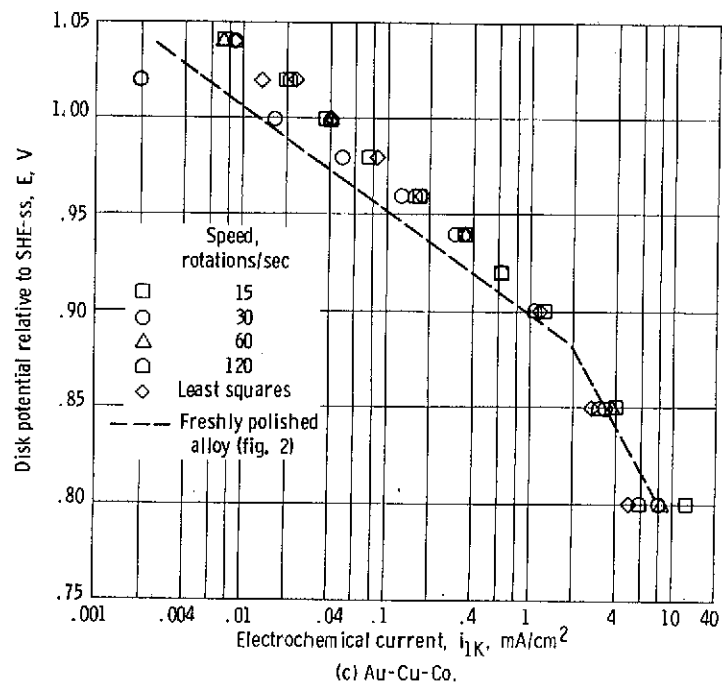


Figure 3. - Concluded.

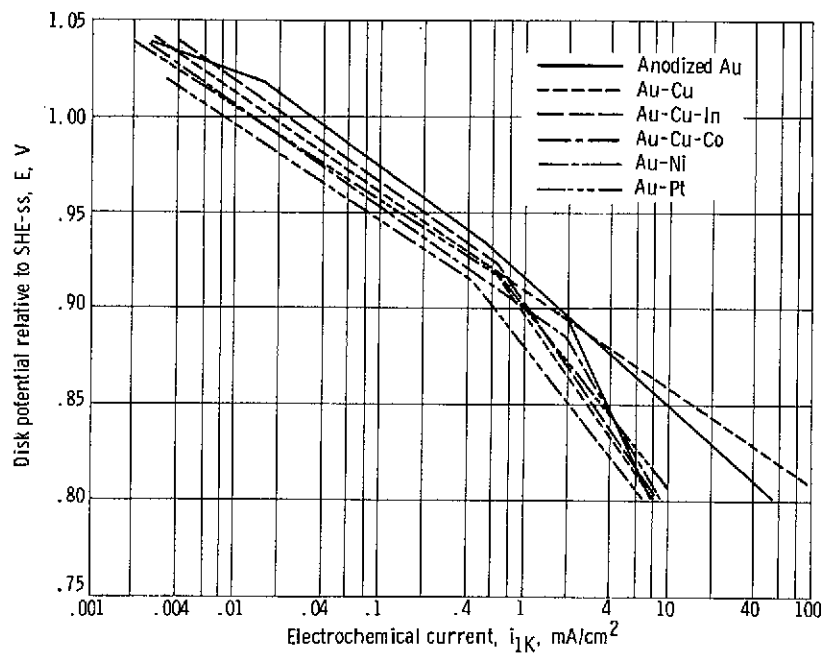
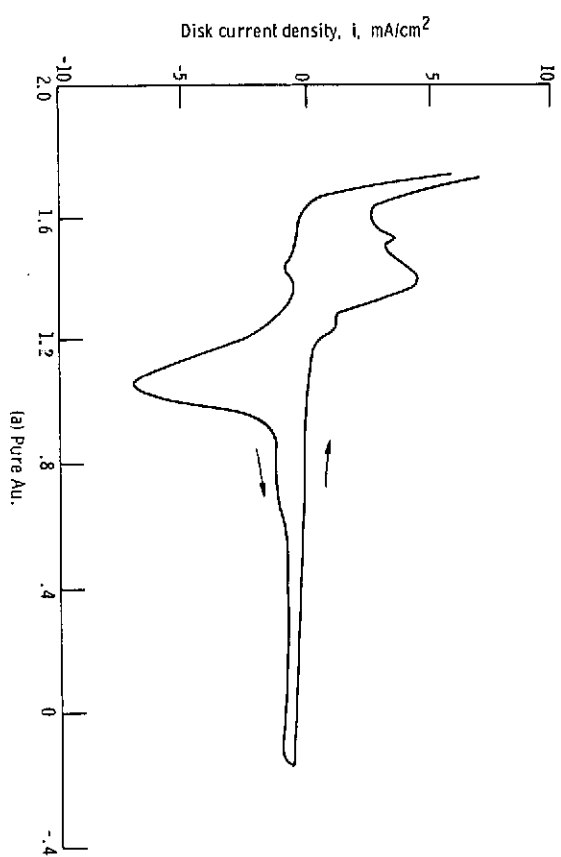
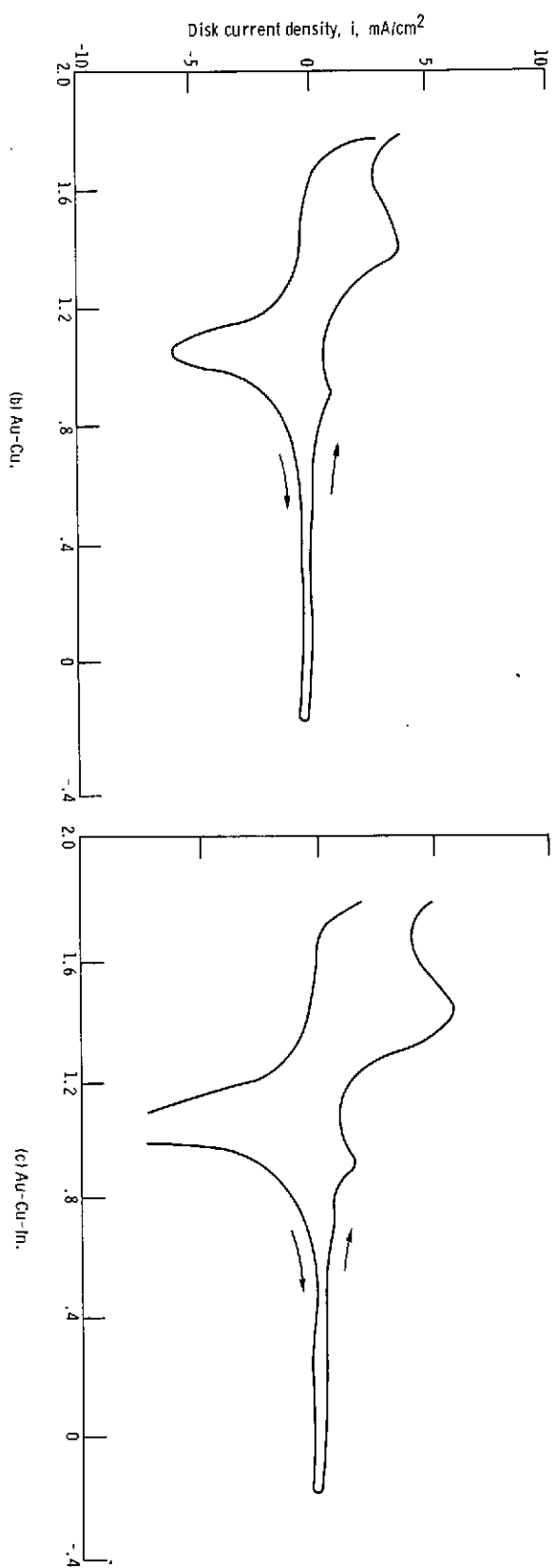


Figure 4. - Tafel plot comparing results for freshly polished alloys with those for anodized pure gold. Anodic-direction sweeps (up from -0.2 V relative to SHE-ss).



(a) Pure Au.



(b) Au-Cu.

(c) Au-Cu-In.

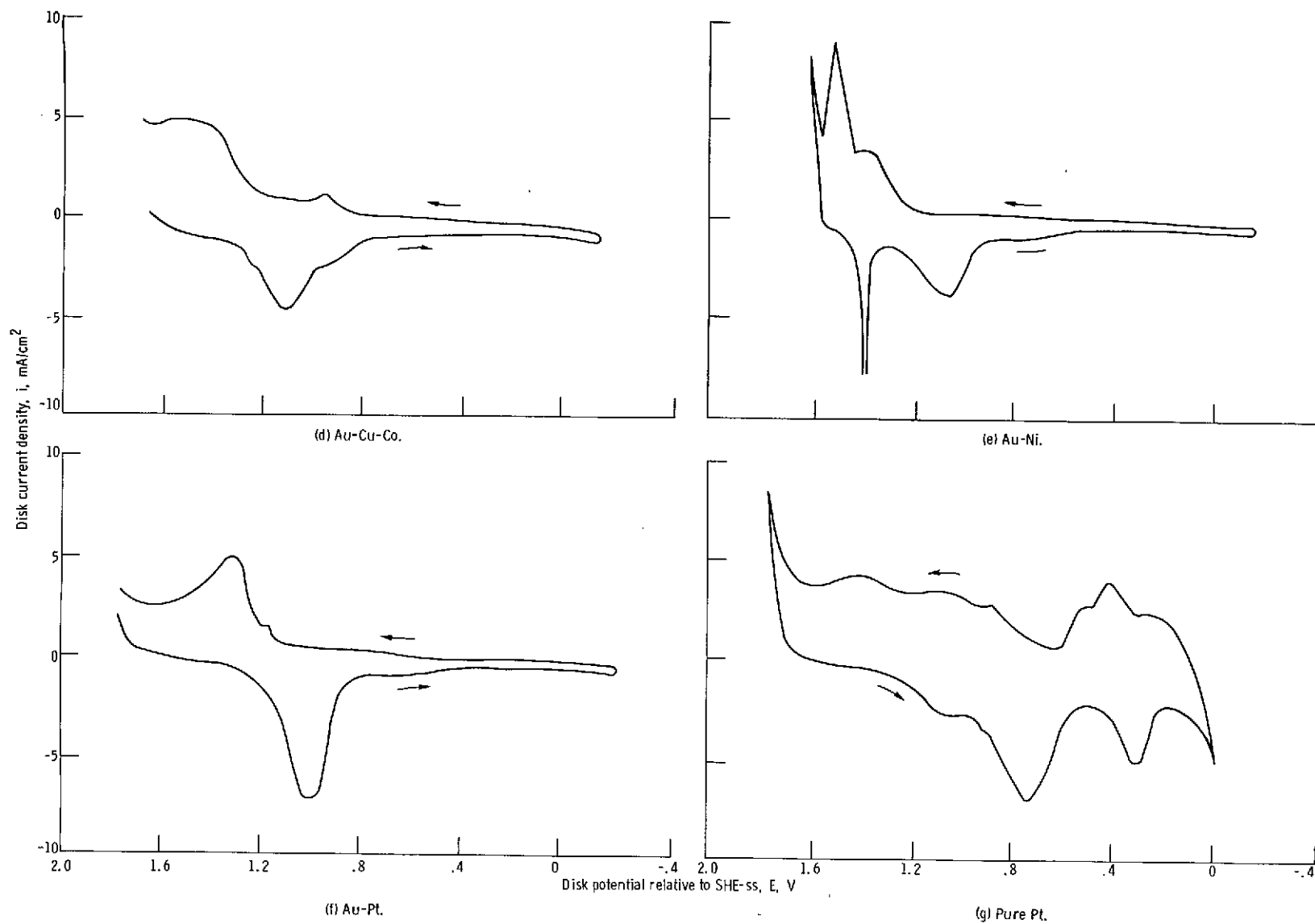


Figure 5. - Rapid-sweep voltammograms. Speed, 60 rotations per second; sweep speed for all metals except Pt, 2 volts per second; sweep speed for Pt, 3.2 volts per second.